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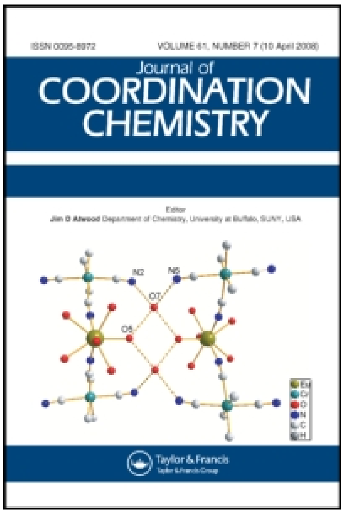

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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M. Villagrán[a]; J. P. Muena[a]; G. Ferraudi[b]; J. H. Zagal[a]; J. Costamagna[a]
[a] Faculty of Chemistry and Biology, Universidad de Santiago de Chile, Santiago, Chile [b] Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, USA

To cite this Article Villagrán, M. , Muena, J. P. , Ferraudi, G. , Zagal, J. H. and Costamagna, J.(2009) 'Electrochemical reduction of S(IV) species in aqueous medium by glassy carbon electrodes modified with polymeric copper(II)tetra-aza-annulene complexes', Journal of Coordination Chemistry, 62: 1, 141 — 149

To link to this Article: DOI: 10.1080/00958970802474771

URL: http://dx.doi.org/10.1080/00958970802474771

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Journal of Coordination Chemistry
Vol. 62, No. 1, 10 January 2009, 141–149

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Electrochemical reduction of S(IV) species in aqueous medium by glassy carbon electrodes modified with polymeric copper(II)tetra-aza-annulene complexes

M. VILLAGRÁN†, J.P. MUENA†, G. FERRAUDI‡, J.H. ZAGAL†
and J. COSTAMAGNA*†

†Faculty of Chemistry and Biology, Universidad de Santiago de Chile, Santiago, Chile
‡Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, USA

(*Received 6 May 2008; in final form 21 July 2008*)

The electrocatalytic reduction of SO_2 in aqueous media was studied as a function of the pH at a glassy carbon electrode modified with poly[Cu(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annulene] film. The best amperometric response was obtained at $pH = 1$ and the activity decreased upon pH increasing. The SO_2 reduction potential in this condition was shifted ca. 220 mV in the anodic direction compared to the value observed in bare glassy carbon. The Tafel slope, $278.64\,mV\,dec^{-1}$, and the charge transfer coefficient, 0.18, are consistent with some interaction between SO_2 and the modified electrode. The amperometric response is linear up to a 0.1 mM SO_2 concentration, the detection limit being 0.02 mM under optimized conditions.

Keywords: SO_2 reduction; Glassy carbon modified electrodes; Electrocatalysis; [Cu(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annulene]

1. Introduction

The transformation of S(IV) plays an important role in environmental atmospheric chemistry, for example acid rain, as well as in several systems of biochemical interest [1–7]. The S(IV) species, such as sulfite and sulfur dioxide, are traditionally used in consumable products and beverages to prevent oxidation and bacterial growth [8–10]. Nevertheless, these preservatives can cause bronchitis, pneumonia and even breath paralysis on individuals who are hypersensitive.

In recent decades, many researchers have studied the determination of S(IV) for purposes such as environmental pollution, occupational safety, the control of beverage quality and industrial waste substances [8].

Methods of determination of S(IV) include iodimetry, gas chromatography, ion chromatography, conductimetry, fluorimetry, chemiluminescence, and electrochemical methods [10]; the last is fast, sensitive and convenient compared to the others.

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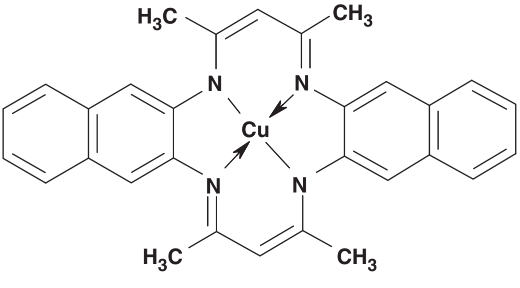
*Corresponding author. Email: juan.costamagna@usach.cl

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802474771



Cu(II)tmdnTAA

Figure 1. Molecular structure for [Cu(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annulene], [Cu(II)tmdnTAA].

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$SO_2 \cdot xH_2O$ is the main species in strongly acidic medium and can be reduced by two electrons. HSO_3^- is the predominant species at $pH = 4$ and can also be reduced with exchange of two or four electrons [11].

Chemically modified electrodes (CME) have acquired great potential and applications during the last years. Recently, a number of CME have been used for the determination of S(IV) in different conditions [12–17]. Nevertheless, the development of low cost, sensitive, portable, and reliable devices for S(IV) determinations is still a challenge.

This manuscript describes the electrocatalytic reduction of SO_2 and HSO_3^- in acidic media using a glassy carbon electrode modified with poly[Cu(II)tmdnTAA] film (figure 1). This modified electrode presents a very high amperometric response as well as a lowering of the sulfur dioxide or bisulfite reduction potential in acidic media compared to values observed with bare glassy carbon.

2. Experimental

2.1. *Chemicals*

[Cu(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annulene] complex, [Cu(II)-tmdnTAA], figure 1, was synthesized and characterized as previously described [18, 19]. Sodium sulfite (Merck, p.a.) was used without further purification. All solutions were prepared using deoxygenated and doubly distilled water. All other chemicals were of analytical grade and used as provided. A homemade Britton Robinson buffer was used in each voltammetric experiment.

2.2. *Apparatus*

Electrochemical measurements were performed with a Princeton Applied Research Potentiostat/Galvanostat PAR-173, a digital Coulometer PAR-179, coupled to a Universal Programmer PAR-175, and a Graphtec X-Y recorder WX4301. Cyclic voltammetry experiments were carried out in a one-compartment, three-electrode glass cell. A poly[Cu(II)-tmdnTAA]/glassy carbon modified electrode was used as working electrode. The auxiliary electrode was a platinum wire. All potentials were measured *versus* a Ag/AgCl/KCl(saturated) reference electrode.

2.3. *General procedures*

H_2SO_4 solution adjusted to $pH = 1.0$ was used as test solution. In each voltammetric experiment, sulfur dioxide was generated *in situ* by addition of the appropriate amount of solid sodium sulfite into the test solution in a hermetic glass cell. The same voltammetric response was obtained for H_2SO_4 solution saturated by SO_2 gas, therefore SO_2 is the unique species in these conditions.

2.4. *Preparation of poly[Cu(II)tmdnTAA]/glassy carbon modified electrode*

Figure 2(a) shows a series of cyclic voltammograms recorded during formation of poly[Cu(II)-tmdnTAA] film over glassy carbon electrode surface from 0.001 M solutions of [Cu(II)-tmdnTAA] and 0.1 M of $(C_2H_5)_4NClO_4$ in CH_3CN. The increase of the current in each cycle in the voltammetric response indicates formation of the conducting poly[Cu(II)-tmdnTAA] film over the glassy carbon electrode. After 50 repetitive cycles between −0.1 and 1.1 V, *versus* Ag/AgCl, the modified electrode was thoroughly rinsed with de-ionized water followed by washing with methanol, and de-ionized water again.

Figure 2(b) shows the voltammetric response of the poly[Cu(II)tmdnTAA] film over a glassy carbon electrode in 0.1 M solution of $(C_2H_5)_4NClO_4$ in CH_3CN. The results show that the poly[Cu(II)-tmdnTAA] film was stable and electrochemically active after repetitive cycles.

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3. Results and discussion

3.1. *pH effect on the catalytic currents and potential for the electrocatalytic reduction of S(IV) species*

The influence of solution pH on the catalytic currents and potentials was assessed by examining the electrode response in Britton Robinson buffer, $1 < pH < 6$ as shown in figure 3. The curve Ip_c *versus* pH shows that electrocatalytic reduction increases at lower pH values. Considering the equilibrium shown in equation (1), the modified electrode is more sensitive to the presence of SO_2 than HSO_3^- or SO_3^{2-}.

$$SO_3^{2-} + 2H^+ == HSO_3^- + H^+ == SO_2 + H_2O \tag{1}$$

Figure 3 shows that in the same pH range the peak potential of the catalytic reduction shifts in the anodic direction, as previously observed by Compton and co-workers for SO_2 reduction at a glassy carbon and copper electrodes [8, 9]; the optimum conditions to study the electrocatalytic reduction of SO_2 over poly[Cu(II)tmdnTAA]/glassy carbon electrodes is in H_2SO_4 solution adjusted to $pH = 1.0$.

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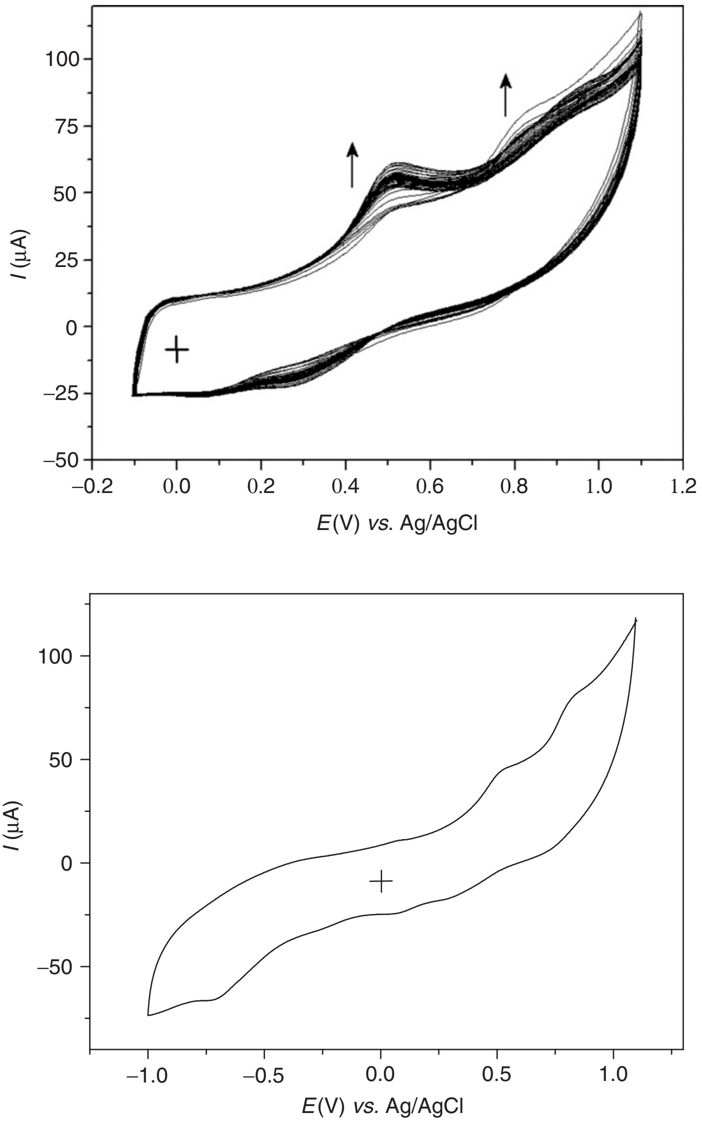

Figure 2. (a) Voltammetric response during poly[Cu(II)tmdnTAA] film formation over glassy carbon electrode surface; (b) voltammetric response of the poly[Cu(II)tmdnTAA] film over glassy carbon electrode in 0.1 M solution of $(C_2H_5)_4NClO_4$ in CH_3CN. Scan rate: 100 mV s^{-1}.

3.2. *Electrocatalytic reduction of SO_2 at pH = 1.0 at poly[Cu(II)tmdnTAA]/glassy carbon modified electrode*

Figure 4 shows cyclic voltammograms recorded at a poly[Cu(II)tmdnTAA]/glassy carbon modified electrode in the presence of 4 mM SO_2 in sulfuric acid solution at pH = 1.0, compared to bare glassy carbon electrode in the same conditions. The observed current increase, about 70%, and the reduction potential shift in the anodic direction, ca. 220 mV, are typical for electrocatalytic processes. This process is verified

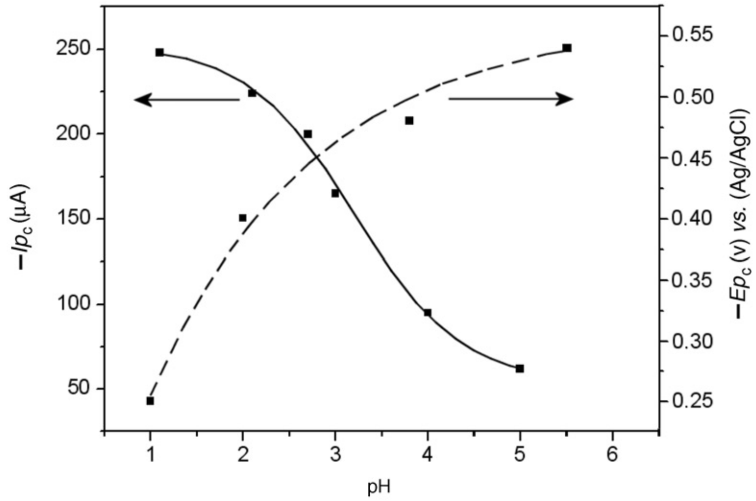

Figure 3. Variation of the catalytic current and reduction potential for S(IV) species at different pH values.

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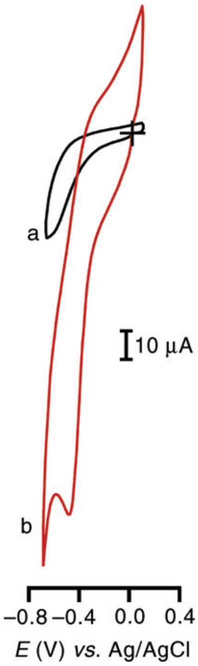

Figure 4. Cyclic voltammograms for SO_2 reduction over, (a) bare glassy carbon electrode, (b) poly[Cu(II)tmdnTAA]/glassy carbon electrode.

in the potential region where copper(II) in the electropolymerized complex is reduced to copper(I) [19b].

Figure 5 shows the current–potential curves for the modified electrode at different scan rates. Inset (a) of figure 5 shows a plot of Ip_c *versus* $v^{1/2}$. The linearity suggests a

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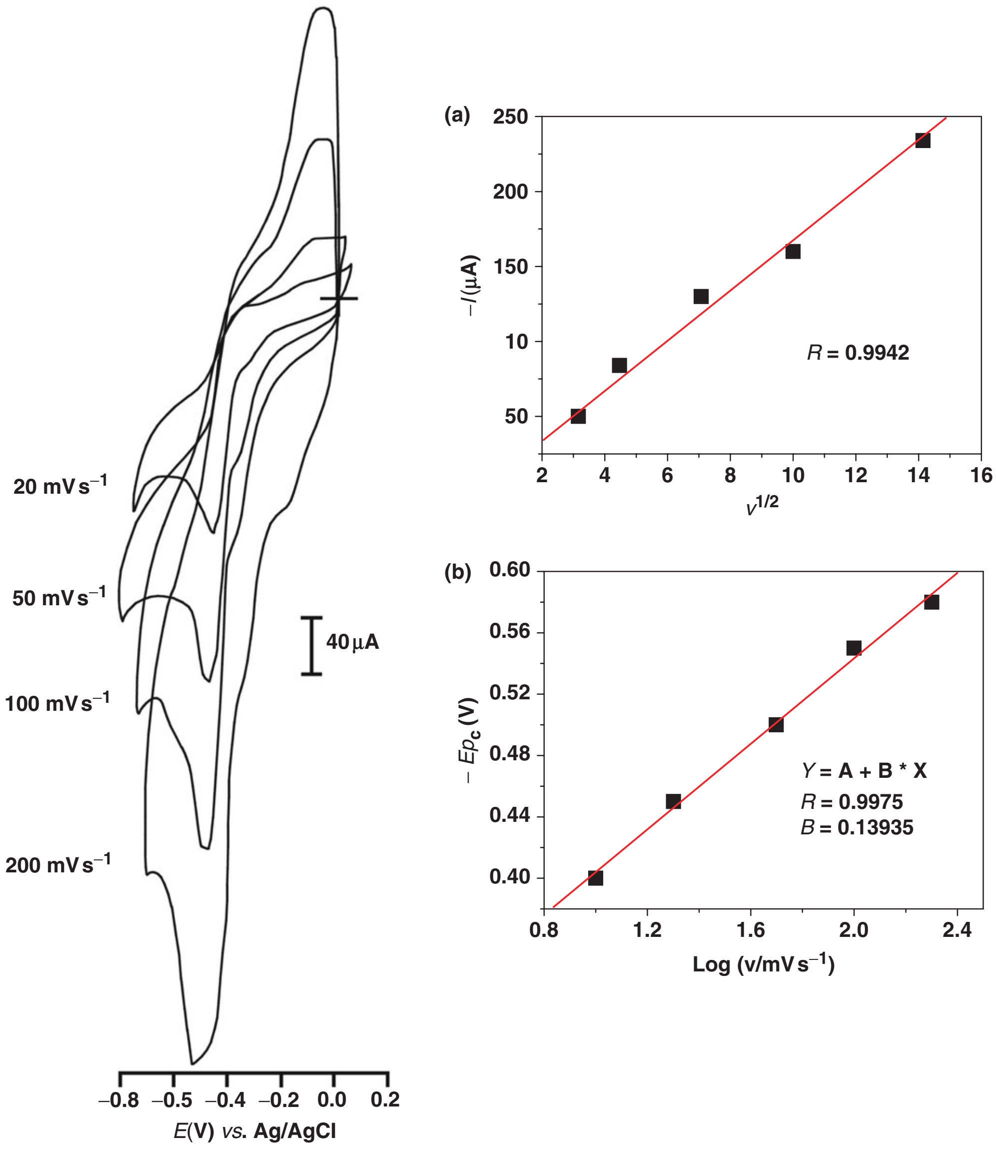

Figure 5. Voltammetric response at different scan rates, for SO_2 reduction over poly[Cu(II)tmdnTAA]/glassy carbon modified electrode. (a) $-Ip_c$ *vs.* $v^{1/2}$; (b) $-Ep_c$ *vs.* log v, graphics.

diffusion process of SO_2 from the bulk solution to the CME surface. Similar voltammograms have been obtained for sulfite solution at $pH = 1.0$, confirming that $SO_2 \cdot xH_2O$ is the active species [11]. Inset (b) of figure 5 shows a plot of $-Ep_c$ *versus* $\log v$. From this graph a Tafel slope, $b = 268.74\,mV\,dec^{-1}$, and a charge transfer coefficient, 0.18, are obtained. These values are in agreement with those obtained from Tafel graphs $-Ep_c$ *versus* $\log I$ from current–potential curve at $10\,mV\,s^{-1}$, $b = 270.0\,mV\,dec^{-1}$ and $\alpha = 0.19$, as shown in figure 6. This can be explained in terms of substrate–catalyst interactions, where the substrate binds tightly to the catalyst

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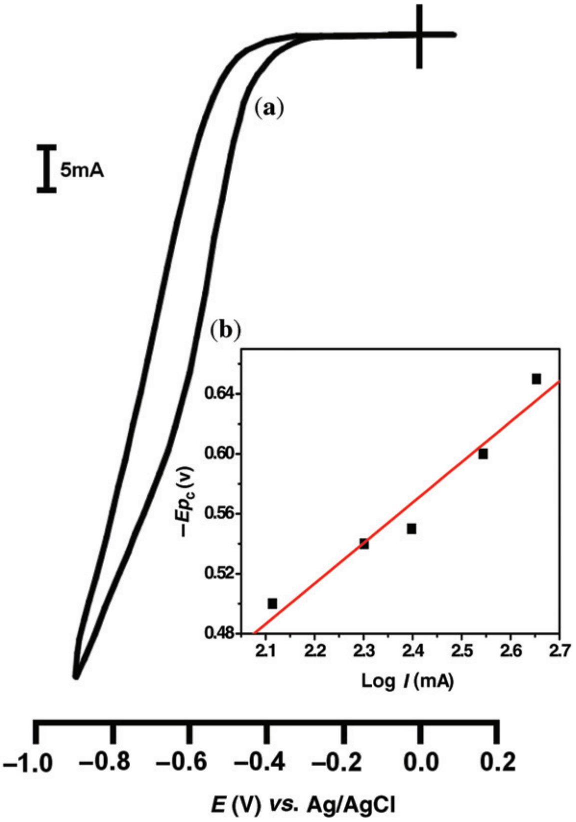

Figure 6. (a) Cyclic voltammogram for SO_2 electroreduction over poly[Cu(II)tmdnTAA]/glassy carbon modified electrode at 10 mV s^{-1}; (b) Tafel graph for SO_2 electroreduction over the CME.

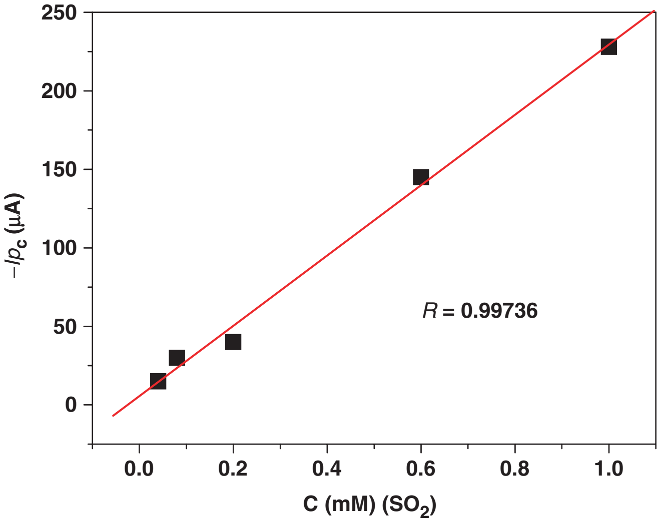

Figure 7. Calibration curve of Ip_c *vs.* SO_2 concentration for poly[Cu(II)tmdnTAA]/glassy carbon modified electrode in H_2SO_4 solution adjusted to pH = 1.0.

during the interaction as a reaction intermediate [20, 21]. Electrolysis experiments for reduction of SO_2 do not show sulfur formation. UV-visible spectrum of the electrolyzed solution shows a band near 350 nm, supporting dithionite formation under the experimental conditions [22], according to the following equations:

$$2\,SO_2 + 2e^- = 2SO_2^{\bullet -} \tag{2}$$

$$SO_2^{\bullet -} + SO_2^{\bullet -} \rightarrow S_2O_4^{2-} \tag{3}$$

3.3. *Amperometric response of the poly[Cu(II)tmdnTAA]/glassy carbon modified electrode*

The amperometric response of the modified electrode obtained under optimized conditions is linear up to 0.1 mM SO_2 as shown in figure 7. The detection limit, calculated from a signal-to-noise ratio equal to 3, is 0.02 mM.

The calibration curve slope suggests a high amperometric sensitivity for SO_2 detection. Figure 4 shows that the current intensity decreases by 70% without catalyst, under the limit of detection in the range studied. Additionally, the potential shifts to more negative values in these conditions.

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4. Conclusions

A stable film composed from electropolymerized [Cu(II)tmdnTAA] over glassy carbon electrode was prepared by cycling the potential working electrode continuously between −0.1 and 1.1 V (*vs.* Ag/AgCl). The modified electrode mediates the electrocatalytic reduction of bisulfite and sulfur dioxide in acidic solution which is strongly dependent on pH. In the optimum experimental conditions, i.e. electropolymerized [Cu(II)-tmdnTAA], hermetic cell, and H_2SO_4 solution adjusted to $pH = 1.0$, the poly[Cu(II)tmdnTAA]/glassy carbon modified electrode shows an amperometric response linear up to 0.1 M SO_2 with a detection limit of 0.02 mM (signal-to-noise ratio equals three). Therefore, this modified electrode can be used as an amperometric sensor for SO_2 determination in aqueous solution.

Acknowledgments

This work was supported by CONICYT, FONDECYT, Project #1060030 and DICYT USACH, Project #020743CM.

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